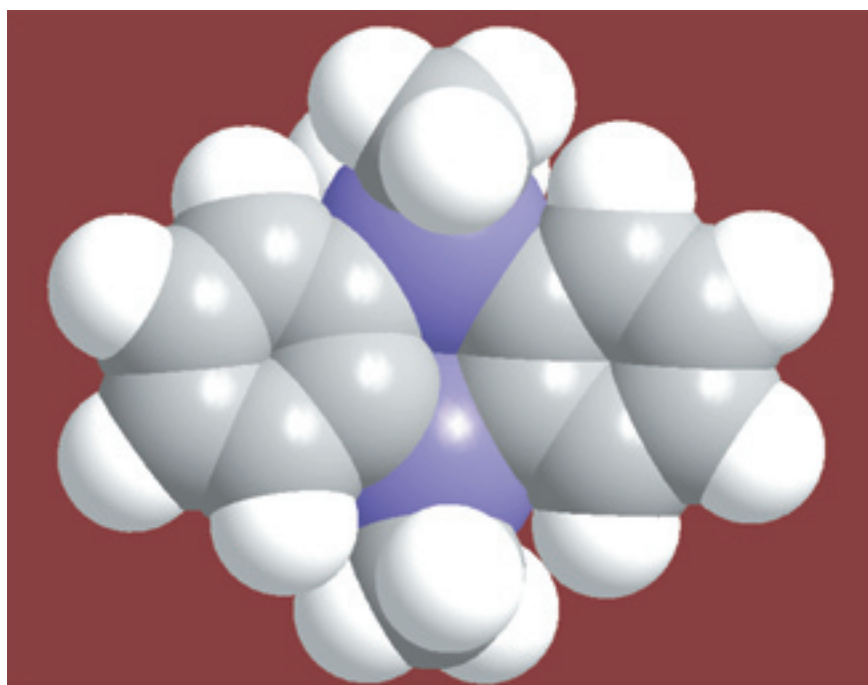


Study of the electronic delocalization in silicon organic derivatives of benzene and their corresponding anion radicals

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Resumen

Se sintetizaron y caracterizaron por IR, RMN-¹H y análisis elemental los compuestos organosilados feniltrimetilsilano (**1**), 1,4-bis(trimetilsilil)benceno (**2**), difenildimetilsilano (**3**) y 1,1',2,2'-dibenzobis(dimetilsilano) (**4**) y se redujeron a los correspondientes aniones radicales organosilados: (trimetilsilil)feniluro de potasio (**1a**), 1,4-bis(trimetilsilil)feniluro de potasio (**2a**), dimetilsilidifeniluro de potasio (**3a**), 1,1',2,2'-bis(dimetilsililfeniluro) de potasio (**4a**). El estudio de deslocalización electrónica se realizó por técnicas de espectroscopía ultravioleta (UV) y de impedancia compleja. La espectroscopía UV evidenció un desplazamiento batocrómico en el siguiente orden: aniones radicales organosilados, organosilados precursores y carbonados análogos, consistente con la delocalización electrónica. Por espectroscopía de impedancia

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cia, se obtuvo información acerca del tipo de impedancia y de la magnitud de la conductividad *dc* para compuestos carbonados como para organosilados y aniones radicales organosilados, ubicando a los organosilados derivados del benceno y a sus correspondientes compuestos reducidos en el rango de los semiconductores y a los carbonados análogos en el de los no conductores.

Palabras clave: organosilanos derivados de benceno, aniones radicales organosilanos, impedancia compleja, deslocalización electrónica

Abstract

The silicon organic compounds phenyltrimethylsilane (**1**), 1,4-bis(trimethylsilyl)benzene (**2**), diphenyldimethylsilane (**3**) y 1,1',2,2'-dibenzobis(dimethylsilane) (**4**) were synthesized and characterized by IR, NMR-¹H and elemental analysis. They were also reduced to the corresponding silicon radical anions: Potassium trimethylsilylphenylide (**1a**), Potassium 1,4-bis(trimethylsilylphenylide) (**2a**), Potassium dimethylsilyl-diphenylide (**3a**), Potassium 1,1',2,2'-bis(dimethylsilylphenylide) (**4a**). The electronic delocalization study was made by UV spectroscopy and complex impedance. By UV spectroscopy evidence was found a bathochromic shift in the following order: silicon radical anions, organosilicon and the analogous carbonate precursors, which is consistent with the electronic delocalization. By impedance spectroscopy, information about the type of impedance and the magnitude of the *dc* conductivity for the carbonates and silicon com-

pounds, as well as their silicon radical anions were obtained. These results allowed us to identify the silicon derivatives of benzene and their corresponding reduced compounds in the range of the semiconductors and those of the analogous carbonates in the non conducting materials.

Key words: silicon- organic compounds, silicon radical anions, complex impedance, electronic delocalization.

1. Introduction

Silicon belongs to the 14th group and has empty *d* orbitals which enable it to form a donor bond (d-p) π with groups that have multiple bonds or pair of unshared electrons^{1,2}.

It is known from spectroscopic studies that silicon bonded to aromatic nuclei shows some degree of expansion of the conjugated system in planar molecules. It was observed that the *p*-band exhibits a shift toward the visible region when compared to similar organic compounds³.

A reasonable explanation of this spectroscopic evidence is that *d* silicon orbital introduces a decrease in the energy required for the electronic jumps within the molecular orbitals of the corresponding compounds².

On the other hand, the chemistry of organic-silicon compounds is important due to its use in organic synthesis and in material science as a promising organic semiconductor².

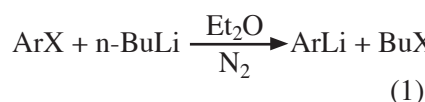
This paper deals with a comparative study of charge transport in organic compounds with and without organosilicon composition by impedance spectroscopy in order

to understand better their electrical characteristics.

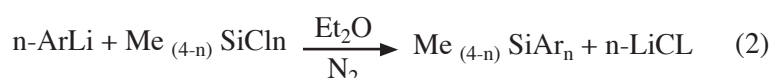
2. Experimental methods and results

The synthesis of the silicon radical anions that were derived from benzene was carried out by the following steps²:

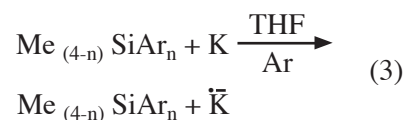
1. **Litiation** by performing the interchanging metal-halogen reaction:



2. **Sililation** by performing a metathesis distributing reaction to form the Si-C bond :



3. **Reduction** to gain an extra electron:



According to equation (1), the ArLi were obtained under an inert atmosphere.

Equation 2 shows the synthesis of the compounds (1), (2), (3), (4), from which the radical anions (1a), (2a), (3a), (4a) were obtained (equation 3).

The IR spectra were recorded with a Perkin Elmer 599 B spectrometer by using nujol as a disperser agent. Table 1 shows the results for the characteristic IR bands where it appears the vibrations that includes methyl and phenyl characteristic groups only.

Table 1. IR bands in cm^{-1} . The number in parenthesis indicates the number of bands.

Group assigned	1	2	3	4
Absorption				
C-H aromatic	3000 (1)	3000 (1)	3000 (1)	3000 (1)
Asymmetrical band of methyl	2964 (1)	2924 (1)	2960 (1)	2960 (1)
Banda symmetrical methyl	2872 (1)	2874 (1)	2900 (1)	2900 (1)
Sobretones region of substituted aromatics	2000-1665(2) ^e	2000-1700(2) ^d	2000-1600 (2) ^e	2000-1600(2) ^e
C=C of ring	1625,1470 (2)	1625, 1590, 1480 (3)	1600, 1470 (2)	6000, 1470 (2)
Si-R deformation symmetrical	1250 (1) ^b	1240 (1) ^b		
(CH ₃) _n of silicon	847,4, 763.3 (2) ^f	847, 763 (2) ^f	854.7, 800 (2) ^g	(1) ^g
Si-Ph	1449, 1123, 694, 740.7 (4)	1449, 1120, 694, 740 (4)	1440, 110, 69, 740 (4)	1580, 1428, 1125, 694 (4)
C-H aromatic substituted	710, 770 (2) ^e	810 (1) ^a	710, 770 (2)	780 (1) ^e

1 phenyltrimethylsilane, 2 1,4-bis(trimethylsilyl)benzene, 3 diphenyldimethylsilane y 4 1,1,2,2-dibenzobis(dimethylsilane)

^a 1,4-disubstituted ^b, R: CH₃, ^c monosubstituted ^d, 1,2-disubstituted ^e, n=3 ^f, n=2.

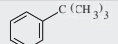
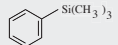
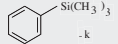
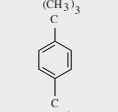
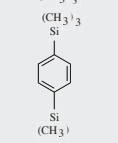
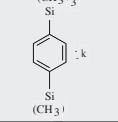
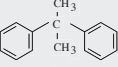
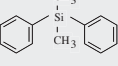
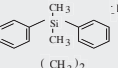
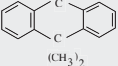
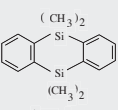
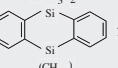
The NMR- ^1H spectra of the samples were recorded with a NMR spectrometer, 90 MHz. All the spectra for the silicon organic compounds showed two characteristic signals: one of them between 0-0.7 ppm with respect to that of the tetramethylsilane; shifted to high field in comparison with those of the methyl bonded to carbon due to the fact that silicon is less electronegative than carbon, so the singlete indicates that the protons are of the same class (methyl). The second signal in the spectra is in the region where the aromatic compounds being resonants, that is, between 7-8 ppm. From their integrations, the number of the aromatic protons for each aliphatic proton is calculated. For example, the spectra for (CCl_4) showed the following chemical shifts (ppm): 0.5 ($\text{Si}(\text{CH}_3)_3$); 7~8.4 (*m*-aromatic). By integration (5:3), it is concluded that there were 10 aromatic protons and six aliphatic. Whence, this compound corresponds to dimethyldiphenylsilane (**3**).

The electronic spectra were recorded with a UV-Vis 160 spectrometer (1100-200 nm) using cells covered with septum.

Electrical conductivity of the samples was measured by impedance spectroscopy using a Hewlett-Packard 4274A LCR meter in the 100 Hz ~ 100 KHz frequency range. The cell used was a classical two-electrode cell. Two identical platinum plates (surface area: 1 cm^2) were used as electrodes and the distance between them was kept to 1.0 cm.

The impedance spectra were analyzed by least square methods in order to find the fitting curves of the $\text{Re}Z$ and $\text{Im}Z$ data points. From an equivalent electrical circuit that better represented the impedance diagram of the cell, the low frequency resistance of the samples and the

Table 2. UV bands in nm for silicon, carbonates and anion radicals compounds.

NAME	STRUCTURE	λ BAND	α Bands
Tert-butylbenzene		215	258
Phenyltrimethylsilane		224	260
Potassium Trimethylsilylphenylide		233	260
1,4-di-tert-butylbenzene		228	319
Potassium 1,4-phenylbis(trimethylsilane)		240.5	319.5
1,4-bis(trimethylsilyl)phenylide		243.5	319.5
Diphenyldimethylmethane		208	259
Diphenyldimethylsilane		216.5	261.0
Potassium Dimethylsilyl-diphenylide		224.0	259.0
Dihydroanthracene		203	258
Diphenylbis(dimethylsilane)		215	258
Potassium 1,1,2,2-bis(dimethylsilyl)phenylide		225	258

corresponding d.c. conductivities at room temperature were determined. The impedance data was recorded at $V_{pp1} < 100$ mV to prevent any side reaction⁴.

Representative impedance diagrams $-\text{Im}Z$ vs. $\text{Re}Z$, for dimethyl diphenylsilane, trimethylphenylsilane, tetramethyldiphenyl-disilane in frequency range 100 Hz ~ 100 KHz and at room temperature are shown in figures 1-5. All these diagrams are better represented by a semicircle which corresponds to an equivalent circuit of a resistance R in parallel with capacitance C (R

being the bulk sample's resistance and C the geometric capacitance of the cell). This behaviour was consistently shown by all the two Pt electrode cells tested in which different kind of organosilicon compounds were used as electrical conductors.

From the intercept of the semicircle with the real axis of the complex impedance plane (which occurs as the frequency tends to zero) were calculated the sample's resistance R and its d.c. conductivity by using $\sigma = l / (RA)$, where A is the electrode's area and l the distance between them. The R and σ values for the samples studied are listed in Table 3.

3. Discussion

The observed impedance behaviour (semicircle-type shape) of the diagrams indicates a prevailing non-blocking electrode situation with infinitely rapid discharge of one mole charged species at the electrodes⁴. So, we argue that the conductivity is mostly electronic not only in reduced compositions of the sample with potassium, but also in the parent silicon compound.

By comparing the conductivity of each reduced composition with its corresponding parent compound, a much higher value is observed for the reduced one due to the extra electron in its radical anion. Thus, it is the number of delocalized elec-

trons in the region of each molecular group which appears to control the conductivity. There are also delocalized electrons in the silicon parent compound since its conductivity has several order of magnitudes higher than its corresponding non-silicon organic compound (benzene).

The rather larger increase of the conductivity in silicon organic compounds, might be attributed to the hybridization of the silicon p -states with its more delocalized empty d -states. These extended (p - d) π bonds build up the conduction path or favouring a hopping migration of the charge carrier which is characteristic of doped semiconductors. In the hopping mechanism, it is assumed that the charge carriers move along one site onto another. Also, in this case the band conduction mechanism is absent because the extended states are too far away from the Fermi level.

4. Conclusion

The silicon organic phenyltrimethylsilane (**1**),

1,4-bis(trimethylsilyl)benzene (**2**), diphenyldimethylsilane (**3**) y 1,1',2,2'-dibenzobis(dimethylsilane) (**4**) and their corresponding anion radicals: potassium (trimethylsilylphenylide) (**1a**), potassium 1,4-bis(trimethylsilylphenylide) (**2a**), potassium dimethylsilyl-diphenylide (**3a**), potassium 1,1',2,2'-bis(dimethylsilylphenylide) (**4a**), were synthesized and characterized by spectroscopic techniques as IR, RMN-¹H and UV.

By comparative studies of the electronic delocalization of the organic compounds through the empty d -orbitals in the silicon derivatives of benzene by UV spectroscopy, a bathochromic shift is observed in the following decreasing ordering: the silicon anion radicals, the silicon precursor and the analogous carbonates. This observation is consistent

Table 3. Resistance and *dc* conductivity data for the compounds studied.

Compounds	$R(\Omega)$	$\sigma(\Omega \text{ cm}^{-1})$
Potassium Trimethylsilylphenylide	292.7	$3.41 \cdot 10^{-3}$
Potassium 1,1,2,2-bis(dimethylsilylphenylide)	241.0	$4.14 \cdot 10^{-3}$
Potassium Dimethylsilyl-diphenylide	1079.0	$0.93 \cdot 10^{-3}$
Potassium 1,4-bis(trimethylsilylphenylide)	300	$3.33 \cdot 10^{-3}$
Phenyltrimethylsilane	8000.0	$1.25 \cdot 10^{-4}$
1,1,2,2-bis-dibenzodimethylsilane	3281.0	$3.04 \cdot 10^{-4}$
Dimethyldiphenylsilane	8400.0	$1.19 \cdot 10^{-4}$
1,4 bis-trimethylsilylbenzene	8000.0	$1.25 \cdot 10^{-4}$
Benzene	20000.0	$5 \cdot 10^{-5}$
Toluene	48930.0	$2.04 \cdot 10^{-5}$
p-Xylene	162000	$6.17 \cdot 10^{-5}$

with the electronic delocalization as well as the number of the resonant structures of the silicon anion. As a whole, four resonant structures are observed for the compounds **1a**, **2a** y **3a**. However, six resonant structures are observed for the compound **4a**.

The impedance spectroscopy results first indicate that the organic compounds based on silicon and their corresponding radical anions exhibit a greater capacitive reactance component of the impedance as a consequence of their higher charge storage capacity due to their empty orbital. On the other hand, the analogous carbonate compounds exhibit a greater resistance component in the impedance indicating an electronic type of conduction. By comparing the corresponding resistance values, the carbonates compounds behaves as non-conducting organic materials, while the silicon as semiconductors.

We have found a correspondence between the delocalization of the electron status and the electrical conductivity in organic molecular compounds with silane group (planar arrangements). The rather large increase of the conductivity when the molecular group accepts an extra electron, adds direct evidence of the delocalized nature of the electron states that participate in the conduction mechanism.

Procedure

0.07 moles of bromobenzene were dissolved in anhydrous ethylether (free of peroxides) and 0.07 moles of n-butyl-lithium 2.5 M dissolved in hexane were added under N₂ atmosphere at 0 °C. The mixture was kept in reflux for two hours. Then, 3.5 mL (0.07 moles) of dimethylchlorosilane dissolved in ethylether and the mixture was kept at reflux for 24 hours at room temperature.

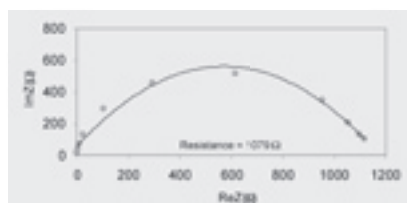


Figure 1. Typical complex impedance plot for a sample of Potassium dimethylsilyl-diphenylide **3a**. Im Z(ω) vs Re Z(ω), where $\omega = 2\pi f$ (f in Hz) at T=300K. Resistance = 292.7 Ω .

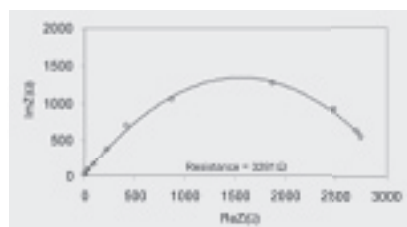


Figure 2. Idem for 1,1',2,2'-dibenzobis(dimethylsilane) **4**.

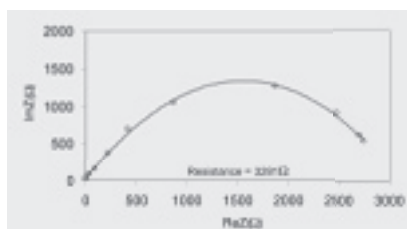


Figure 3. Idem for Potassium (trimethylsilyl-phenylide) **1a**.

A Hydrolysis using a 10% H₂SO₄ solution was performed and the mixture was thoroughly washed with distilled water and the organic layer was removed and dried with anhydrous Na₂SO₄. The organic solvent was extracted at reduced pressure and the raw material was purified by column chromatography over silica-gel using hexane as a solvent.

The compound was then treated with metallic potassium in THF just distilled to yield the anion radical under vacuum conditions and at room temperature. A colour change indicated the formation of the product.

The same procedure and measurements were conducted for trimethylphenyl-silane, and tetramethyldiphenyl disilane. A yellow-

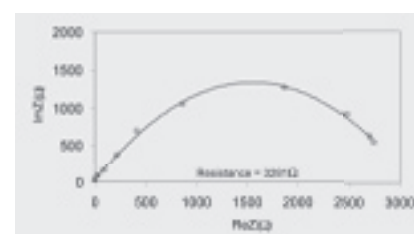


Figure 4. Idem for dimethylphenylsilane.

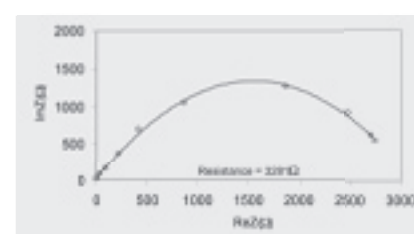


Figure 5. Idem for Potassium 1,1',2,2'-bis(dimethylsilylphenylide) **4a**.

ish liquid was collected having a density of 0.9824 g/mL. ☼

Acknowledgements

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